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# ELECTROCHEMISTRY LABORATORY

Professor Dr. N. Sato, Assistant Professor Dr. M. Seo
Mr. M. Sakashita, Mr. R. Nishimura and Miss C. Miura

***Students***

Y. Yomura. I. Iwata, H. Gotoh, S. Maruoka and N. Sato

Passivity of iron-group metals and alloys in aqueous solution is being investigated in this laboratory. Detailed information about the structure and composition of passive films on iron has been collected by a sophisticated cathodic reduction technique combined with ellipsometer and chemical analysis. In addition, quantitative depth profiles of passive films on iron and iron-base alloys have been obtained by means of Auger electron spectroscopy. Also, an ellipsometric spectroscopy technique having been developed in this laboratory is being used for the studies on the passivity and pitting corrosion of iron and iron-base alloys. Besides, studies on anodic oxidation of molybdenum and copper are commenced from this year. In pararell with the passivity study, anionic- and cathodic-selective properties of metal hydroxides membranes are being continuously investigated with the aim of understanding the role of metal hydroxides formed on metals as corrosion products in the passivity and pitting corrosion.

Professor Sato attended NACE Corrosion Research Conference held in Houston, Texas, USA. Dr. Ohtsuka having belonged to this laboratory as a ph. D. student went abroad to study at Professor Heusler's laboratory, Technische Universität Clausthal, West Germany from May 1976 for two years.

Four foreign scientists visited this laboratory: Professor J. O'M. Bockris (School of Physical Science, The Flinders University of South Australia), Professor T. N. Rhodin (School of Applied and Engineering Physics, College of Engineering, Cornell University, N. Y., USA), Dr. L. Rédey (Department of Applied Chemistry, Faculty of Chemical Engineering, Technical University of Budapest, Budapest, Hungary) and Dr. V. S. Fomenko (Institute of Materials Problems, Academy of Science UKR, Kiev, USSR).

## Oral Presentations

Effect of Precipitated Hydrous Metal Oxide Membranes on Metal Corrosion —Selective Ion Permeability and Diffusion Potential—; M. Sakashita and N. Sato: 11th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb. 1976.

Passive Films on Chromium in Acid Solutions; R. Saito, K. Kudo and N. Sato: *ibid.*, Feb. 1976.

Anodic Oxidation of Cobalt in Neutral Solutions; N. Sato, K. Kudo and T. Ohtsuka: 1976 NACE Corrosion Research Conference, Houston, Texas, USA, March 1976.

AES Analysis of Surface Composition of Fe–Ni Alloys; M. Seo and N. Sato: Spring Meeting of the Japan Institute of Metals, Apr. 1976.

Structure and Property of Anodic Oxide Films; N. Sato: 14th Seminar of Corrosion Engineering, Apr. 1976.

Effect of Molybdate Ion on Selective Ion Permeability of Precipitated Hydrous Iron Oxide Membrane; M. Sakashita and N. Sato: 43rd Annual Conference of the Japan Electrochemical Society, Apr. 1976.

Effect of Precipitated Hydrous Metal Oxide Membranes on Metal Corrosion —Selective Ion Permeability and Diffusion Potential—; M. Sakashita and N. Sato: 3rd Annual Conference of the Japan Society of Corrosion Engineering, May 1976.

Selective Ion Permeability of Precipitated Hydrous Iron Oxide Membrane; Y. Yomura, M. Sakashita and N. Sato: *ibid.*, May 1976.

Passive Films on Cobalt; T. Ohtsuka, K. Kudo and N. Sato: *ibid.*, May 1976.

Effect of Oxidation Time on the Composition of Passive Films on Iron in Neutral Solutions; R. Nishimura, K. Kudo and N. Sato: *ibid.*, May 1976.

Auger Electron Spectroscopy of Passive Films on Chromium; M. Seo, R. Saito, K. Kudo and N. Sato: *ibid.*, May 1976.

Passive Films on Iron Surface; N. Sato: 14th Kaya Conference, Aug. 1976.

Surface State of Electrode and Interface Reaction —Similarity of Metal Corrosion and Catalyst—; N. Sato: Symposium of the Japan Chemical Society, Aug. 1976.

Passive Films on Iron in Phosphate Solutions; R. Nishimura, K. Kudo and N. Sato: 35th Fall Meeting of the Japan Chemical Society, Aug. 1976.

Selective Ion Permeability of Precipitated Hydrous Ferric Oxide Membrane in Neutral Solutions; Y. Yomura, M. Sakashita, K. Kudo and N. Sato: *ibid.*, Aug. 1976.

Electrochemical Dissolution Mechanism of Metal Oxides and Potential Distribution at Metal Oxide/Solution Interface; M. Seo and N. Sato: *ibid.*, Aug. 1976.

Effect of Solution pH on the Selective Ion Permeability of Precipitated Hydrous Ferric Oxide Membrane; M. Sakashita and N. Sato: *ibid.*, Aug. 1976.

Stability of Anodic Oxide Films on Cobalt; T. Ohtsuka and N. Sato: 27th Meeting of International Society of Electrochemistry, Zurich, Switzerland, Sept. 1976.

# HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

Prof. Dr. K. Nishida, Assist. Prof. K. Atarashiya,
Dr. T. Narita and Mr. K. Sugawara

***Students***

H. Kinoshita, M. Takahashi, K. Taniguchi, S. Okazaki,
H. Senzaki, Y. Iwami, S. Karasawa, K. Sakurai,
T. Matsunaga, M. Yamada and T. Nishizawa

The laboratory is investigating the dry corrosion of metals and alloys. The diffusion in metals is also being investigated by means of a metallic vapor technique on the basis of corrosion and protection researches. A light beam furnace (L. B. F.) is found very useful in the synthesis of some high-temperature refractory oxides by fusion.

At present the research is being carried out on the followings :

(1) Oxidation of Co-based Cu and Mn alloys ; The effect of the oxygen pressure on oxidation rates was further investigated to other kinds of Co-based alloys and the composition profile in the oxide solid solutions, (Co, Me) O, was obtained. Some modifications of the original theory were made in order that the perfect solution of the equations might be obtained with given values and rather (wide) necessary data could be calculated.

(2) The metallizing of refractory metals and their oxidation ; V metal were metallized with a pack cementation technique as well as a metallic vapor technique and the so-called CVD method was newly tested to be applicable.

(3) Interdiffuison in Ni–Al and Co–Al systems ; Ni and Co metals were exposed to Al vapor to obtain mutual diffusion coefficients in their intermediate phases by using the Al vapor prepared from the two-phase powders.

(4) Many kinds of mixtures of $Ta_2O_5$ and $Al_2O_3$ were prepared

by fusion with L. B. F. and their electric conductivities ($\sigma$) were measured at 900°∼1500°C. The mixture with 50∼30 at % $Al_2O_3$ showed a significant decrease of ($\sigma$) corresponding to the formation of Z phase ($TaAlO_4$). Other mixtures ($Ta_2O_5$-$SiO_2$, $Ta_2O_5$-$Cr_2O_3$) were also prepared and their electric conductivities were examined.

## Oral Presentations

1. Fe concentration profile in the oxides formed on low Fe-Co alloys at high temperatures; K. Kimura, T. Narita and K. Nishida: 11th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1976.
2. The Oxygen Pressure Dependence of High-Temperature Oxidation of Low Fe-Co Alloys; T. Narita and K. Nishida: The Spring Meeting of the Japan Institute of Metals, April, 1976.
3. Study On Interdiffusion in $\alpha$ solid solution of a Ni-Zn System; T. Yamamoto, K. Nishida and T. Takashima: *ibid.*, April, 1976.
4. Interdiffusion in $\Gamma$ Phase of an Fe-Zn System; H. Suzuki and K. Nishida: *ibid.*, April, 1976.
5. Some Experiments on the Synthesis of Ferrous Sulfide Single Crystal; M. Yamada, T. Narita and K. Nishida: The Hokkaido Section Meeting of JIM and ISIJ, June, 1976.
6. Surface Treatment and Anti-Oxidation Property of Ta and Other Refractory Metals; K. Nishida: Seminar sponsored by the Hokkaido Section of JIM, June, 1976.
7. Mössbauer Effect of Ferrous and FeS-MnS Sulifides; H. Ōhashi, T. Tani, T. Narita, K. Nishida and T. Morozumi; The Fall Meeting of Japan Chemical Society, Aug., 1976.
8. Interdiffusion in $\beta$ and $\beta'$ Phases of a Ni-Zn System; H. Kinoshita, T. Narita and K. Nishida: The Fall Meeting of Japan Institute of Metals, Oct., 1976.
9. Synthesizing of Ta-Containing Oxides and Measurement of Their Electric Conductivities: K. Taniguchi, T. Narita and K. Nishida: *ibid.*, Oct., 1976.
10. Stress Dependence of Oxidation Behavior of Pure Ni Metal at High Temperatures; M. Takahashi, T. Narita and K. Nishida:

*ibid.*, Oct., 1976.

11. Some Considerations on the Oxide Scale Structure formed on Alloys ; T. Narita and K. Nishida : *ibid.*, Oct., 1976.
12. High-Temperature Sulfurization of Fe–Mn Alloys ; K. Nishida: "U.S.-Japan Joint Seminar on Defects and Diffusion in Solids" in Tokyo, Oct., 1976.
13. Calculation of Cation Distribution in Oxide Scale formed on Co–Ni Alloys (II) ; T. Narita and K. Nishida : The Hokkaido Section Meeting of JIM and ISIJ, Nov., 1976.
14. High-Temperature Sulfurization of Iron and Steel ; K. Nishida: Symposium on "High Temperature Corrosion and Its Protection" sponsored by the Japan Institute of Metals, Dec., 1976.

# ELECTROMETALLURGY LABORATORY

Prof. Dr. T. Ishikawa, Dr. T. Notoya,
Dr. T. Sasaki and Mr. S. Konda

### *Students*

H. Ichikawa, T. Abe, A. Suzuki, H. Okuyama, K. Sugita,
K. Kasama, J. Asano, A. Kanazawa,
T. Komatsubara and H. Tanda

Research subjects in this laboratory are as follows.

(1) Concerning the low temperature electro-refining and electro-winning of aluminum in the molten salt mixtures of aluminum chloride and sodium chloride at about 200°C, the anodic behaviors of aluminum scraps, of insoluble anode and the behavior of deposited aluminum on the nickel cathode are being investigated.

(2) Laboratory scale tests in the single cells and the bipolar electrode cells for electro-winning of liquid aluminum are being carried out by using alkali and alkali-earth chlorides molten salts containing aluminum chloride in the temperature range from 700° to 800°C. The electrolytic conductivities of these molten salts and the solubilities of aluminum metal to these molten salts are also being measured in this temperature range.

(3) Concerning the electrolytic treatments of waste water from metallurgical processes, various bipolar cells are developed and various fundamental studies are also in progress.

(4) In order to elucidate the effects of surface preparation, pretreatment and history on the anodic passivation process of austenitic stainless steels, electrochemical studies are in progress by means of potential recyclic sweep methode and ESCA analysis.

(5) In addition an investigation of the corrosion inhibition mechanisms of copper and copper base alloys is being undertaken with heterocyclic organic compounds. It is intended to study the relationships among structures of inhibitor films, nature of oxides

formed on the metals and the crystallographic orientations of the substrates.

Dr. Notoya was invited by the Gordon Research Conference on Corrosion held at Colby-Sawyer College in New Hampshire, U. S. A. in July for presentation of recent work on corrosion inhibitors. On the way to New Hampshire he visited the Professor F. Habashi's laboratory at the Laval University in Quebec, the Professor D. Piron's laboratory at Ecole Polytechnique in Montreal, and the Professor G. W. Poling's research group at the University of British Columbia in Vancouver.

## Oral Presentations

Effect of Heat Transfer on Pitting Corrosion of Aluminum: M. Konno and T. Ishikawa: 11th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1976.

Corrosion Protection of Copper with Benzotriazole; T. Notoya and G. W. Poling: *ibid.*, Feb., 1976.

Film Thickness of Cu-Benzotriazolate and Corrosion Inhibition of Copper; T. Notoya and G. W. Poling: 43rd Spring Meeting of Chemical Society of Japan, April 1976.

The Role of Cuprous Oxide in Protection of Copper; T. Notoya and G. W. Poling: 43rd Meeting of Electrochemical Society of Japan, April, 1976.

Electrolysis of Aqueous Solution by Bi-polar Electrode Cell —Properties of the Cell packed in Layers with Graphite and Alumina Beads alternately—; T. Sasaki, K. Sekizawa and T. Ishikawa: *ibid.*, April 1976.

Electrolysis of Aqueous Solution by Bi-polar Electrode Cell —Performance of the Cell packed with Mixture of Graphite and Alumina Beads—; T. Sasaki, S. Nishiuchi and T. Ishikawa: *ibid.*, April 1976.

Anodic Dissolution Behaviors of Al-Si-Fe Alloys in the Low Temperature Molten Salts containing Aluminum Chloride; O. Yamamoto and T. Ishikawa: *ibid.*, April 1976.

Fundamental Studies on ALCOA New Smelting Process (Part 2)

Effect of $AlCl_3$ Concentration on Current Efficiency and Purity of electrodeposited Aluminum; T. Abe, S. Konda and T. Ishikawa: *ibid.*, April 1976.

Effect of Heat Transfer on Pitting Corrosion of Austenitic Stainless Steels; T. Ishikawa: Annual Conference of the Japan Society of Corrosion Engineering, May 1976.

Pitting Corrosion Test of Aluminum under Heat Transfer Conditions; T. Ishikawa and M. Konno: *ibid.*, May 1976.

Surface Topography and the Corrosion Inhibition Mechanisms of Copper and Copper Alloys; T. Notoya and G. W. Poling: The Gordon Research Conference on Corrosion, New Hampshire, U. S. A., July 1976.

Relationship between Aluminum Electrode Potential and Composition of Molten Salt Mixtures containing Aluminum Chloride and Alkali Chlorides; T. Ishikawa: 35th Fall Meeting of Chemical Society of Japan, Aug., 1976.

Topography of Cu-Benzolate Films formed on Copper; T. Notoya and G. W. Poling: *ibid.*, Aug., 1976.

Corrosion Protection of Copper and Copper Alloys with Collectors for Mineral Processing; T. Notoya: *ibid.*, Aug., 1976.

On Packed Bi-polar Electrode Cell for Waste Disposal in Metal Plating Industry; T. Sasaki and T. Ishikawa: *ibid.*, Aug. 1976.

Electrowinning of Liquid Aluminum by using Funnel Pile Type Bipolar Electrode Cell (Part 1) Correlation between Shape of Electrode and Cell Efficiency; T. Ishikawa: 10th Symposium on Molten Salt Chemistry, Nov., 1976.

Electrowinning of Liquid Aluminum by using Funnel Pile Type Bipolar Electrode Cell (Part 2) Some Problems on the Cell Operation and Results directly observed in the Cell: K. Sugita, S. Konda and T. Ishikawa; *ibid.*, Nov. 1976.

Dissolution Characteristics of Crude Aluminum Anode in the Low Temperature Molten Salts containing Aluminum Chloride: O. Yamamoto and T. Ishikawa; *ibid.*, Nov. 1976.

Fundamental Studies on ALCOA New Smelting Process (Part 3)

Effect of Temperature and Cation in Molten Salts on the Cell Voltage and Current Efficiency: T. Abe, S. Konda, T. Ishikawa and H. Ichikawa; *ibid.*, Nov. 1976.

# PHYSICAL METALLURGY LABORATORY

Prof. Dr. T. Takeyama, Assist. Prof. Dr. T. Shibata
Dr. H. Takahashi, Mr. M. Hachinohe,
and Mr. H. Ohtaki

***Students***

M. Uetsuka, N. Yokoya, T. Sawada, S. Ohnuki, T. Niiyama,
T. Hara, T. Edamura, H. Murakami, T. Matsuhashi,
Y. Tetsuka, H. Hirose and M. Arigane

Structural damage in metals and alloys induced by irradiation of neutron in the nuclear reactor could be simulated by using accelerated electron and ions. In this laboratory, 650 kV high voltage electron microscope is used to irradiate the material and examine its structural changes in situ. Accelerated $C^+$ ions at 200 kV are another source of irradiation. Void formation in pure iron was found to depend on the temperature during irradiation of $C^+$ ions. Possible interaction of interstitial carbon atoms with defects produced by irradiation was suggested. Hydrogen blistering in pure iron and iron-nickel alloys is being studied to clarify the precipitation mechanism of hydrogen in metals. Electrochemical condition of stress corrosion cracking of stainless steel in concentrated chloride solution at high temperature is analysed by using the high speed straining method. Stress corrosion cracking of titanium in iodine-alcohol system has been studied. Transition in fracture mode from intergranular to transgranular cracking is demonstrated to occur with change in stress level, oxygen content in titanium, and carbon number of solvent alcohol. Statistical nature of pit intiation for stainless steel and high nickel alloys is analysed based on the stochastic theory.

Professor Takeyama joined the USA-JAPAN Seminar on HVEM at Hawaii, USA, and presented a paper.

## Oral Presentation

Morphology of Fractured Surface of Titanium in Stress Corrosion Cracking; T. Shibata and T. Takeyama: The Hokkaido Section Meeting of Japan Society for Electronmicroscopy, Feb., 1976.

Electron Irradiation Damage in Nickel; T. Swada, H. Takahashi and T. Takeyama: *ibid.*, Feb., 1976.

Martensitic Transformation of Type 304 Stainless Steel and Polarization Characteristics; S. Ohnuki, T. Shibata, and T. Takeyama: The 11th Annual Meeting of The Corrosion Research Association in Hokkaido, Feb., 1976.

Straining Electrode of Iron and Nickel; T. Shibata and T. Takeyama: The Spring Meeting of the Japan Institute of Metals, April, 1976.

Construction of Multichannel Pitting Corrosion Testing Apparatus and its Applications; T. Shibata, T. Takeyama, and T. Wakabayashi: The 43rd Annual Meeting of Japan Electrochem. Soc., April, 1976.

Study of Stress Corrosion Cracking of Stainless Steels by means of Straining Electrode Method; T. Shibata: Annual Conference of the Japan Society of Corrosion Engineering, May, 1976.

Effect of Plastic Deformation on Hydrogen Blistering in Iron; H. Takahashi, T. Hara, and T. Takeyama: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, Jun., 1976.

Ultra-High Temperature Tensile Testing Apparatus and High Temperature Tensile Strength of Tantalum; T. Takeyama and G. Tomita: The Seminar on Refractory Metals and Materials sponsored by the Japan Institute of Metals, Jun., 1976.

Effect of Neutron Irradiation on Mechanical Properties of Iron; T. Takeyama: The Seminar on the Cooperative Research sponsored by The research Institute for Iron, Steel and Other Materials, Tohoku University, Jun., 1976.

Effect of Plastic Strain on Hydrogen Precipitation in Iron; T. Hara, H. Takahashi, and T. Takeyama: The Fall Meeting of the Japan Institute of Metals, Oct., 1976.

Direct Observation of Initial Stage of Hydrogen Precipitation in Iron; H. Takahashi and T. Takeyama: *ibid.*, Oct., 1976.

Stress Corrosion Cracking of Titanium in Methanol-Iodine Solution; T. Shibata and T. Takeyama: *ibid.*, Oct., 1976.

Ultra-High Temperature Tensile Testing Apparatus and its Applications; T. Takeyama and G. Tomita: *ibid.*, Oct., 1976.

Solvent Effect on the Stress Corrosion Cracking of Titanium; T. Shibata and T. Takeyama: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, Nov., 1976.

Precipitation Phenomena in Vanadium-Carbon Alloys; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid.*, Nov., 1976.

Effect of Neutron Irradiation on Mechanical Properties of Iron; N. Yokoya, H. Takahashi, T. Takeyama, and H. Kayano: *ibid.*, Nov., 1976.

Effect of Pre-strain on the Void Formation of Nickel by Electron Irradiation; T. Swada, H. Takahashi, and T. Takeyama: *ibid.*, Nov., 1976.

Metallurgical Application of High Voltage Electron Microscope —Effects of Precipitation—; T. Takeyama: The Symposium of Japan Society for Electromicroscopy, Nov., 1976.

Electron Irradiation Damage and Precipitation; T. Takeyama and H. Takahashi: The Seminar on Metallurgical Applications of In-Situ Experiments in HVEM sponsored by the Japan Institute of Metals, Dec., 1976.

Effect of In Situ Heating on $\varepsilon$-Carbide Irradiated by means of HVEM; T. Takeyama and H. Takahashi: The USA-JAPAN Joint Seminar on HVEM, Dec., 1976.

# ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Dr. H. Tamura, Dr. H. Takahashi
Dr. H. Konno, Mr. Y. Otake, Mr. N. Kameda
and Miss Y. Ikeno

### *Students*

M. Koda, M. Oshima, M. Takimoto and K. Go

At present, research being conducted is concerned with anodic oxidation of metals, cathodic deposition of metals, X-ray photoelectron spectroscopy for metal surfaces and oxygenation of metallic ions in solution. We are most interested in understanding the nature of solid/aqueous solution interphases and the mechanism of the reactions occuring there. Nagayama attended the 27th annual meeting of the International Society for Electrochemistry (Zurich) and the Corrosion Science Symposium (Leeds) in September 1976. On his way to Zurich, he was invited to the University of Szeged, Hungary, to discuss problems on passivity with Dr. Rauscher and his colleagues.

Main topics of our research are:

(1) Formation of 'barrier-type' anodic oxide films on aluminium: Oxide films are anodically formed in neutral borate and phosphate solutions. Dissolution behaviour, structure and composition of the films are being examined by chemical analysis, electron-microscopy and ESCA techniques.

(2) Determination of the porosity of anodic oxide films on aluminium: When Al specimens preliminarily anodized to form porous oxide films in acid solutions are re-anodized in a neutral boric acid-borate solution at a constant c. d., oxide formation occurs both at the barrier layer/solution and oxide/metal interphases, corresponding to the migrations of $Al^{3+}$ and $O^{2-}$ ions through the barrier layer. In this investigation, the porosity of the porous oxide is being determined from the analysis of the voltage-time curve

obtained in the re-anodization experiment, by using the transport numbers of these ions estimated by electron microscopy on sections of films.

(3) Transport numbers for $Al^{3+}$ and $O^{2-}$ ions during anodizing of Al in acid solution: Transport numbers for $Al^{3+}$ and $O^{2-}$ ions across the barrier layer of porous oxide during anodizing of Al in $H_2C_2O_4$ solutions are being calculated from the dissolution data on the basis of the following assumptions, (a) $Al^{3+}$ ions transferred into the sloution without forming the oxide at the barrier layer/solution interface and (b) part of the oxide formed at the barrier layer/metal interface, due to $O^{2-}$ migration, dissolves into the solution to produce pores. The figure obtained for the transport number of $Al^{3+}$ is in the range 0,25∼0·50 and it was found to increase with decreasing current and rising temperature.

(4) Air-oxidation of ferrous ion in neutral solutions: Effects of Fe (III)-hydroxide, the reaction product, and coexisting anions such as $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$, $H_2PO_4^-$ and $BO_2^-$ have been examined with the hope of understanding the rusting process in iron. Dissolution characteristics of the formed Fe (III)-hydroxide is being examined in a tartaric acid solution as functions of the conditions of the air-oxidation (the solution pH, concentrations of co-existing anions and temperature).

(5) XPS-studies on metal surfaces. X-ray photoelectron spectroscopy with argon ion sputtering is being applied to investigate the passive films on iron formed in a neutral boric acid-borate solution. The same technique is going to be applied to clarify the composition of chromic-chromate films formed on various metals during chromium plating.

## Oral Presentations

Catalytic Effect of Hydrous Fe (III)-oxide on the Air-oxidation of Ferrous Ion; K. Takahashi, H. Tamura and M. Nagayama: The 1976 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chemical Soc., Jan. 1976.

Determination of $CN^-$ by Silver-Titration; N. Nishitani, H. Konno and M. Nagayama: *ibid.* Jan. 1976.

Adsorption of Pyrophosphate on Cu during Cu Plating from Cu-Pyrophosphate Solutions; H. Konno and M. Nagayama: The 11th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb. 1976.

Anodic Formation of Oxide Films on Al in Neutral Borate Solutions; H. Takahashi and M. Nagayama: The 43rd Annual Meeting of the Japan Electrochemical Soc., Apr. 1976.

Comparison of the Catalytic Effects of Various Hydrous Fe (III)-oxides on the Air-oxidation of $Fe^{2+}$ ions; H. Tamura, K. Takahashi and M. Nagayama: *ibid.* Apr. 1976.

Effect of Ammonia on Copper Depositon from Pyrophosphate Baths; H. Konno and M. Nagayama: *ibid.* Apr. 1976.

Structure and Dissolution Behaviour of Anodic Oxide Films on Aluminium; M. Koda, H. Takahashi and M. Nagayama: The 1976 Summer Meeting of the Hokkaido Sections of the Japan Chemical Soc. and Japan Soc. for Anal. Chem., July 1976.

Formation and Dissolution-Mechanism of Anodic Oxide Films on Aluminium; M. Nagayama: Symposium on Surface Treatment of Aluminium, Sponsored by the Japan Light Metal Soc., Aug. 1976.

Dissolution Behaviour of Hydrous Fe (III)-oxides in Acidic Solutions; H. Tamura, M. Oshima and M. Nagayama: The 35th Annual Meeting of Japan Chem. Soc., Aug. 1976.

Electrochemical Behaviour and Structure of Anodic Oxide Films Formed on Aluminium in a Neutral Borate Solution; M. Nagayama and H. Takahashi: The 27th Meeting of the International Soc. for Electrochem., Zürich, Sept. 1976.

Oxygenation of $Fe^{2+}$ in Neutral Solutions; M. Nagayama: The 17th Corrosion Science Symposium, Leeds, Sept. 1976.

Effect of Cathodic Pretreatment on the Passivation of Iron in Neutral Solutions; A. Rauscher, H. Konno and M. Nagayama: *ibid.* Sept. 1976.

# ENGINEERING MACHINERY MATERIALS LABORATORY

Prof. K. Nagaoka, Assist. Prof. T. Noguchi,
Mr. N. Shiramine, Mr. M. Sōma and Mr. M. Fujita

***Students***

Y. Sugawara, Y. Matsumoto, S. Ōyatsu, N. Suzuki,
M. Matsubara, Y. Murase and T. Yamada

In this laboratory, researches on engineering materials for machinery have been concentrated on the properties of cast iron, such as fracture strength, growth in high temperature and thermal-conductivity. In addition, some examinations are carried steadily on other metals concerning with strength and heat treatment. Recently surface-hardening of sintered iron products has been dealt with a new process. Researches in progress are listed as follows:

(1) According to a stress analysis based on the non-elastic characteristics, the conventional bending strength of cast iron circular plate by center load was formulated as a function of tensile strength and diam.-thickness ratio. Experimental results obtained from some circular plates with various dimension and grade of strength agreed well with the formulated curves.

(2) The fracture strength of rotating cast iron-disks with and without center holes was examined analytically. Non-elastic stress distribution was calculated by the computer matrix method based on the deformation theory. The calculated results showed that the maximum hoop stress decreased and the stress distribution became uniform with increasing the rotating velocity.

(3) Remarkable increase of growth of cast iron observed in dilute oxygen heating-atmosphere was examined again with pre-grown iron in the mixed gases of argon and air. In the atmosphere of 2.5% air the maximum of growth rate was obtained. The most promoting concentration of mixed gases for pre-grown iron was less then that of as-cast iron. The promoting effect in-

creased with increasing heating cycles.

(4) Growth of cast iron was tested in hydrogen atmosphere by cyclic heating to 950°C. Cast iron grew in hydrogen, and the growth was poor in comparison with in air and argon. But in austenite region the growth rate in hydrogen was almost same as that in argon. The difference may be explained in terms of the structural change in grown iron. In hydrogen the matrix was all pearlitic and in argon ferrite was observed around graphite flakes.

(5) Thermal-conductivities of cast iron with various chemical compositions and graphite configurations were measured. After the consideration on the conductivity of metalic matrix, a concept of "form factor" was introduced to analyze the effect of the graphite shape.

(6) Surface-hardening of sintered iron with graphite was tested by the heating in dilute oxygen atmosphere. By quenching after the heating of about half an hour at 900°C, a hardened case of about 2 mm depth with surface hardness of over 500 Hv was obtained. However, because of the troubles on chemical analysis for sintered iron with graphite the mechanism of surface-hardening was not clarified.

(7) Miscellaneous subjects of research are as follows:

a) Low-temperature strength of cast iron.
b) Bending creep of heat-treated steel.
c) Phenomenon of self-carburization in grown cast iron.
d) Micro-particle analysis of graphite phase in grown S. G. iron.

## Oral Presentations

On the Bending Strength of Cast Iron; K. Nagaoka and T. Noguchi: The 2nd Symposium of Japan Foundrymen's Society, Jan. 1976.

On the Bending Strength of Cast Iron Circular Plates; T. Noguchi and K. Nagaoka: The 89th Grand Lecture Meeting of Japan Foundrymen's Society, May 1976.

On the Promoting Effect of Oxygen on the Growth of Cast Iron;

M. Sōma and K. Nagaoka: The 89th Grand Lecture Meeting of Japan Foundrymen's Society, May 1976.

On the Fracture Strength of Rotating Cast Iron Disks; T. Noguchi and K. Matsushita: The 25th Grand Lecture Meeting of The Society of Material Science, Japan, May 1976.

Promoting of Growth in Cast Iron by Heating in Various Atmospheres; M. Sōma and K. Nagaoka: The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1976.

Effect of Non-elastic Characteristics on the Notch and Bending Strength of Cast Iron; K. Nagaoka and T. Noguchi: The Seminar of Impact Strength Committee of The Japan Foundrymen's Society, Aug. 1976.

On the Growth of Cast Iron in Hydrogen Atmosphere; M. Sōma and K. Nagaoka: The 90th Grand Lecture Meeting of Japan Foundrymen's Society: Oct. 1976.

# NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. T. Morozumi, Assist. Prof. H. Ohashi
Dr. T. Mizuno, Dr. M. Moriya, Mr. K. Hirohara
and Mrs. N. Ochiai

***Students***

H. Narita, S. Kato, T. Shindo, M. Otsuka, M. Nabeshima,
Y. Kawaguchi, T. Kurachi, S. Kawakatsu, K. Nakagawa,
T. Otani, T. Aoyama, H. Hayashi, H. Takai
and S. Miyamae

In this laboratory, the research is being carried on the following:

(1) The rate of hydrogen uptake into titanium and zirconium was measured under the conditions of cathodic polarization in various solutions. The hydrogen concentration profile, the thickness of hydride layer and the total amount of absorbed hydrogen were obtained by means of chemical and nuclear chemical analyses. The rate law and the reaction mechanism of hydride formation were discussed on the basis of above observations.

(2) A variety of ferric oxyhydroxides were prepared and calcined at various temperatures. The reductive and non-reductive dissolution rates of these products were measured. Moreover, the Mössbauer spectroscopic and the X-ray diffractive measurements of the oxyhydroxides and its calcined products were made. The change in chemical reactivity by calcination were corelated with the changes of BET areas and the structural changes. The computer treatment of the undefined Mössbauer spectrum data was also investigated.

(3) Electrochemical study on the corrosion of high nickel alloys, such as Hastelloy-C and others, in acidic solutions: The quantitative analysis of dissolved metals, the potentiostatic polarization characteritics, the ultra low-frequency impedance and the ESCA spectrum were measured.

(4) The apparatus of activation analysis was devised for the Hokkaido University 45 MeV electron linear accelerator. Relatively strong activation and high detection level with the thermal neutron flux of about $10^9$ n/cm$^2$. sec, was achieved for various elements by improving the configuration and the materials of the Bremsstrahlung target. The apparatus was utilized mainly for the analysis of metallic materials in connection with the corrosion problems, e. g. the analysis of manganese and other elements in iron and its alloys, gallium in aluminium etc.

(5) Kinetic studies on the further oxidation of uranium dioxide to the higher oxides and on the dissolution of various oxides of uranium in acidic solutions were continued. Although, at present, our studies are limited to the specimen prepared by the decomposition of urany salt, the work will be extended to the sphere-particle specimen made by the Sol-Gel method.

## Oral Presentations

Activation Analysis with a 45 MeV Electron Linear Accelerator Installed at the Hokkaido University; H. Narita, H. Ohashi, T. Morozumi: the 1976 Winter Joint Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Anal. Chem. Soc. Jan., 1976.

Oxidative Reaction Mechanism of Uranium Dioxide; H. Ohashi, H. Hayashi, T. Morozumi: The 1976 Annual Meeting of the Atomic Energy of Japan, March 1976.

Dissolution of Oxides of Uranium in Aqueous Solution of Nitric Acid; S. Kato, H. Ohashi, T. Morozumi: The 35th Fall Meeting of the Japan Chem. Soc., Aug. 1976.

Effect of Thermal History on Oxidation Rate of Uranium Dixide: H. Ohashi, H. Hayashi, T. Morozumi: *ibid.*, Aug. 1976.

Effect of Impurities in Solution upon Electrolytic Hydrogen -uptake into Titanium and Zirconium; T. Shindo, T. Mizuno, T. Morozumi: *ibid.*, Aug. 1976.

Mössbauer Spectra of FeS and FeS–MnS; H. Ohashi, T. Tani, T. Narita, K. Nishida, T. Morozumi: *ibid.*, Aug. 1976.

## VACUUM SCIENCE LABORATORY

Prof. Dr. T. Yamashina, Assis. Prof. Mr. K. Watanabe,
Dr. M. Mohri, Dr. M. Nagasaka (Present address :
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin,
West Germany) Dr. S. Tanaka (Present address :
University of Vermont, U. S. A.) Mr. M. Hashiba,
Mrs. Y. Hirohara and Mr. M. Sasaki

***Students***

M. Yabumoto, H. Kakibayashi, K. Nakamura, M. Nishino,
S. Ito, T. Obata, S. Kato, H. Yagami

In this laboratory, research work on the surface phenomena of solids and vacuum engineering is in progress with the following subjects :

(1) Simultaneous measurement of AES–SIMS–FDS for clean surface of metals and alloys : The structure and property of clean surface of Ni and Cu–Ni alloys are investigated by using a combined system of Auger spectroscopy, secondary ion mass spectroscopy and flash desorption spectroscopy to carry out the elemental analysis, the state analysis and the reaction process, simultaneously.

(2) Reaction kinetics of titanium, zirconium and their alloys with hydrogen, oxygen and nitrogen at very low pressures : Kinetic measurements of metal-gas interactions in the pressure range from $10^{-5}$ to $10^{-7}$ Torr and in the temperature range from 600° to 800°C are being made by means of an ultrahigh vacuum microbalance with high sensibility.

(3) Selective sputtering of binary alloys : Selective sputtering of binary alloys such as Cu–Ni, Ag–Au and etc. is studied by means of Auger spectroscopy utilizing the difference in the escape depth of Auger electrons with different energies.

(4) Surface passivation of semiconductor device : In-depth profiles of passivated films and interface of oxide-metal on GaAs are

compared with those of various oxide films prepared by anodic and thermal oxidation.

(5) Surface study of nuclear fusion materials: Plasma and first wall interactoins have been started recently, especially on the surface phenomena of interactions of carbon and SiC with proton with different energies.

## Oral Presentations

Flash Decomposition of Formic Acid on Ir; M. Noro, K. Watanabe and T. Yamashina: The 1976 Winter Meeting of the Hokkaidp Sections of the Japan Soc. for Anal. Chem. and the the Japan Chem. Soc., Jan., 1976.

Reactivity of Nitrogen in the reactive-sputtered films of iron nitride; Y. Kobayashi, Y. Hirohata, K. Watanabe and T. Yamashina: *ibid.*

Effect of Gamma-ray Irradiation on Catalysis of La-oxide; S. Ozaki, M. Mohri and T. Yamashina: *ibid.*

Formation Process of Chemical Compound Films of Mn prepared by Reactive-sputtering; T. Sasaki, T. Abe and T. Yamashina: The Annual Meeting of Hokkaido Sections of the Japan Society Applied Physics, Feb., 1976.

R. F. Sputtering Process of Cu–Ni Alloys; M. Yabumoto, K. Watanabe and T. Yamashina: *ibid.*

Deposition Process of Films in the Reactive Sputtering (II)-Mo–$H_2$; The 23rd Annual Meeting of Japan Society of Applied Physics; Tokyo, March 1976.

In-depth Profile of Anodic Oxide Films on GaAs by SIMS–AES; T. Yamashina, M. Hashiba, K. Watanabe and H. Hasegawa: *ibid.*

Surface Composition and Segregation Process of Cu–Ni Alloys by Auger Spectroscopy; K. Watanabe, M. Hashiba, Y. Fukuda and T. Yamashina: The 34th Annual Meeting of Japan Chemical Society, Tokyo, Apr., 1976.

Adsorption and Decomposition of CO and $C_2H_4$ on Clean Surface of Cu–Ni Alloys by AES–SIMS: M. Mohri, M. Hashiba, K.

Watanabe and T. Yamashina : *ibid.*

Flash Decomposition of Formic Acid on Ir Clean Surface; K. Watanabe, M. Noro and T. Yamashina; The Annual Meeting of Japan Catalysis Society, Sapporo, Aug., 1976.

AES Study of Surface Composition and In-depth Profile of Clean Cu-Ni Alloys; K. Watanabe, M. Hashiba and T. Yamashina: The 39th Discussion Meeting of Japan Catalysis Society, Sapporo, Aug., 1976.

The Simultaneous Measurement of AES-SIMS-EDS for Adsorption and Desorption on Alloy Surfaces; M. Mohri, M. Hashiba, K. Watanabe and T. Yamashina: The 24th Annual Meeting of Japan Society of Applied Physics, Sendai, Sept., 1976.

In-depth Profile ofPassiv ated Films on GaAs by AES-SIMS (II)-Comparison of Thermal and Anodic Oxidations; M. Hashiba, M. Mohri, K. Watanabe and T. Yamashina; *ibid.*

A Quantitative Analysis of Surface Segregation Cu-Ni Alloys; K. Watanabe, M. Hashiba, M. Mohri and T. Yamashina: The 79th Annual Meeting of Japan Institute of Metals, Sendai, Oct., 1976.

High Pressure DPA-DTA Study of Hydrogen Sorption by Ti; E. Uyeda, S. Uyeda, K. Watanabe and T. Yamashina: *ibid.*

# NONFERROUS EXTRACTIVE METALLURGY LABORATORY

Prof. Dr. T. Tanaka, Assist. Prof. T. Nagai
Mr. H. Kiuchi, Mr. R. Shibayama
and Mr. S. Tasai

### *Students*

K. Nakajima, T. Iwazaki M. Kobayashi, K. Chiba,
K. Kaneko, K. Higashioka ane N. Yamamoto

This laboratory is concerned with basic and applied researches on pyro- and hydro-metallurgical extractions of nonferrous metals.

Researches in progress are concentrated on the following projects:

(1) Researches on hydrogen production from sulfide compounds

a) Reaction between metal sulfides and water vapour at high temperatures. Thermodynamic and kinetic investigations are being made for the production of hydrogen and hydrogen sulfide from sulfide ores.

b) Researches on the production of hydrogen from hydrogen sulfide. Conversion of hydrogen sulfide to hydrogen by molten metals and regeneration of metals from metal sulfides by mutual reaction are being carried out.

$$2Pb(1)+2H_2S \rightleftharpoons 2PbS(s)+2H_2$$

$$PbS+2SO_2 \rightleftharpoons PbSO_4+S_2(g)$$

$$PbS+PbSO_4 \rightleftharpoons 2Pb(l)+2SO_2$$

Cyclic treatments of hydrogen sulifide by combination of following two reactions are also in progress:

$$Fe_3O_4+6HCl+H_2S \rightleftharpoons 3FeCl_2+4H_2O+S^\circ$$

$$3FeCl_2+4H_2O(g) \rightleftharpoons Fe_3O_4+6HCl+H_2$$

(2) Reduction kinetics of metal sulfides by hydrogen. This study is aimed at finding the mechanism of direct reduction of

sulfide ores. Observation of the nucleation and growth of reduced metals by scanning electron-microscope, morphologic characteristics of the metals reduced from sulfides, oxides, chlorides, and sulfates, and vapour phase reduction of metal sulfides being made.

(3) Reduction of metal sulfates by hydrogen. Measurements of reduction rate, identification of reduction products are being made. The mechanism of the formation of metallic copper from $CuSO_4$ at very low temperature, 300°C is also being investigated.

(4) Electrochemical measurements in some pressure hydrometallurgy. The reaction kinetics of the oxygen pressure leaching of sulfide minerals and the hydrogen reduction of metal salts in aqueous solutions are being studied by means of polarization measurements of sulfides and metal electrodes in an autoclave under the conditions of temperature up to 200°C and pressure of 50 kg/cm$^2$.

### Oral Presentations

Feasibility study of the FeS-HCl-$H_2O$ for hydrogen production; R. Shibayama, K. Nakajima and T. Tanaka: The 1976 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Jan., 1976.

A Study for the Thermal Decomposition of Hydrogen Sulfide with Molten Metals; H. Kiuchi, T. Iwasaki, and T. Tanaka: *ibid.*, Jan., 1976.

Fundamental Studies on the Decomposition of $H_2S$ by the Hydro-Metallurgical Reactions; R. Shibayama, K. Nakajima and T. Tanaka: Annual Meeting of the Mining and Metallurgical Institute of Japan, March, 1976.

A Study for the Effective Utilization of Hydrogen Sulfide (II); H. Kiuchi, T. Iwasaki, and T. Tanaka: *ibid.*, Apr., 1976.

Fundamental Studies on the Reaction between Metal Sulfides and Water Vapour at High Temperatures (II); R. Shibayama and T. Tanaka: *ibid.*, March, 1976.

Researches on the Recovery of $H_2$ from $H_2S$ by the Sulfurization of Molten Metals; H. Kiuchi, T. Iwasaki, and T. Tanaka: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute of Japan, Jun., 1976.

Treatment of Arsenic Bearing Solutions by Solvent Extraction; M. Kobayashi, and T. Nagai: The Hokkaido Section Meeting of the Mining and Metallurgical Institute of Japan, Jun., 1976.

A Study for the Thermal Decomposition of Hydrogen Sulfide with Metals (II); H. Kiuchi, T. Iwasaki, and T. Tanaka: *ibid.*, Jun., 1976.

Purification of Copper Electrolyte by Solvent Extraction; T. Nagai, N. Yamazaki, and M. Kobayashi: Fall Meeting of the Mining and Metallurgical Institute of Japan, Oct., 1976.

Recovery of $H_2$ and S from $H_2S$ with Metal Sulfide; H. Kiuchi, T. Iwasaki, and T. Tanaka: The 3rd Symposium on Hydrogen Energy System, Hydrogen Energy Society in Japan, Nov., 1976.

A Decomposition Cycle of $H_2S$ with Ferrous Chloride; R. Shibayama and T. Tanaka: *ibid.*, Nov., 1976.

Non-Ferrous Extractive Metallurgy and Hydrogen; T. Tanaka, H. Kiuchi and R. Shibayama: The 3rd Research Meeting, Hydrogen Energy System Society of Japan, Nov., 1976.

Treatments of Sulfide Ores through Hydrogen; T. Tanaka, H. Kiuchi and R. Shibayama: The 24th Non-Ferrous Extractive Metallurgy Research Meeting, Dec., 1976.

# Deformation of Iron Single Crystal in the Blue-brittleness Temperature Range

H. Takahashi, K. Takahashi and T. Takeyama

Bulletin of the Faculty of Engineering,
Hokkaido University, **80**, 103 (1976)

In order to study the effect of dislocation structures on the temperature dependence of mechanical properties of iron, a single crystal with a [110] axis was extended in a temperature range from room temperature to 300°C and deformation structures were observed by transmission electron microscopy. Serration phenomenon is observed in the stress-strain curves at 200 to 250°C, where a high workhardening rate is shown. In the same temperature range dislocations are multiplied remarkably and the intervals of slip lines as well as those of cell walls which are approximately parallel to the slip plane {112} become smaller than at other temperatures.

These results suggest that the temperature dependence of the work-hardening rate is due mainly to that of dislocation distribution and its multiplication rate, that is, small cell size and high dislocation density give rise to high work-hardening rate in the blue-brittleness temperature range where dynamical strain aging occurs remarkably. (Japanese)

# Irradiation Hardening and Annealing in Irons at a High Neutron Fluence

T. Takeyama, H. Takahashi, N. Yokoya
and H. Kayano

International Conference on Radiation Effects and
Tritium Technology for Fusion Reactors 1975,
Riverside Motor Lodge, Gatlinburg,
Tennessee, U.S.A. October 1-3

The purpose of the present study is to obtain basic information on the irradiation effect of two kinds of iron with different carbon contents; specimen A (Fe-0.002 wt % C), specimen B (Fe-0.012 wt % C). The behavior of the lattice defects occurring due to neutron irradiation was investigated using electron microscopy and mechanical examination.

Following irradiation, specimen A showed voids of about 500 Å in size. The void density obtained through direct observation was about $1.0 \times 10^{14}/\mathrm{cm}^2$. In contrast, in specimen B the void was difficult to observe. It was concluded that for the formation of voids by irradiation, specimens with less carbon atoms were desirable. An intriguing observation obtained through void formation showed that the yield stress of specimen A was higher than specimen B with a high carbon content. The mechanism involved may be closely related to the hardening caused by void formation. (English)

# Effect of Electron Irradiation on Precipitation of Carbon and Nitrogen in Alpha Iron

T. Takeyama and H. Takahashi
International Conference on Fundamental Aspects
of Radiation Damage in Metals, Gatlinburg,
Tennessee, U.S.A. October 5–10, 1975

Vacancies and interstitials were introduced in solution quenched Fe–0.025 wt % C and Fe–0.03 wt % N alloys by aid of electron irradiation in a 650 kV HVEM, and the interaction between the point defects and the solute atoms was studied from the results of aging behavior revealed by the precipitation phenomena. The sequence of precipitation of quench-aging is $\varepsilon$-carbide and cementite for Fe–C alloy and $\alpha''$-nitride and $\gamma'$-nitride for Fe–N alloy. In the irradiated area, however, no visible precipitates appeared on both the aged specimens. As it was certain that mainly a large number of vacancies must remain in the irradiated area, supersaturated carbon of nitrogen atoms are considered to migrate and be trapped by the single vacancies to form C–V pairs or N–V pairs. (C : carbon, N : nitrogen, V : vacancy) Therefore, the precipitation phenomena were prevented by the trapping effect. The dissociation of the C–V pair or N–V pair was observed by the existence of the precipitation in the irradiated area at higher aging temperatures. The detrap temperature of the C–V pair and N–V pair was 240°C and 200°C, respectively. Above these temperatures unually large particles of cementite and smaller particles of $\alpha''$-nitride than those seen in the un-irradiated area were observed. (English)

# Electron Irradiation Damage and Material Science by Means of High Voltage Electron Microscopy

T. Takeyama

Denshi-Kenbikyo (Electron-Microscope) **11,** 21 (1976)

Recent developments of HVEM application for studying the electron irradiation damage in metals and alloys were reviewed. HVEM has advantages of the high stability of accelerating voltage and the high flux of irradiation electrons, so that structural defects could be produced for very short exposure time in easily controlled conditions. Recent results on the formation of defect clusters, an interaction between point defects and dislocations, void formation, and an interaction between point defects and solut atoms were reviewed. Especially, the interaction between solut carbon atoms and vacancies, suppression of the formation of ε-carbide and cementite in Fe–C alloy were discussed. (Japanese)

# On the Bending Strength of Cast Iron Round Bar

T. Noguchi and K. Nagaoka

IMONO, 48, 2 (1976), Feb.

In cast iron, it is well known that the bending strength $\sigma_b$, obtained by the rupture moment and the section modulus, is almost twice the tensile strength $\sigma_t$. In the previous paper, the authors proposed a new theoretical formula, $\sigma_b=(2.0-\sigma_t/100)\times\sigma_t$ ($\sigma_b$, $\sigma_t$ : kg/mm$^2$) for a rectangular beam. But strictly, such a bending strength varies according to the geometry of the cross section of the beam.

In the present paper, the bending strength of round bar was calculated theoretically, taking into consideration the non-elastic stress-strain relationship of cast iron using an electronic computer.

Calculated results showed that the bending strength of a round bar was 10% higher than that of a rectangular beam, independent of the strength and the profile of the stress-strain curve of the material. In effect, a new formula for the estimation of the bending strength, $\sigma_b=1.1\times(2.0-\sigma_t/100)\times\sigma_t$, was obtained for a round bar. The formula was recognized valid after comparing with the experimental values offered by fourteen perfectural industrial laboratories. It was also confirmed experimentally that the as-cast specimens had lower strength and wider scattering range than lathed specimens. (Japanese)

# On the Stress Concentration Factors of Notched Cast Iron

T. Noguchi and K. Nagaoka

IMONO, **48**, 8 (1976) Aug.

Though cast iron is known as a brittle metal, it has low notch sensitivity. In this paper, in order to elucidate the effect of non-elastic behavior on the low notch sensitivity, stress concentration factors in notched cast iron plates were calculated using FEM based on the secant modulus theory.

Non-elastic stress concentration factor $\alpha_c$ of cast iron was equal to the elastic $\alpha$ only in the range of $\sigma_n/\sigma_t \leqq 0.1 \sim 0.2$, where $\sigma_n$ is applied normal stress and $\sigma_t$ is the tensile strength. The higher the tensile strength of cast iron, the wider the stress range where $\alpha_c \approx \alpha$. With increasing $\sigma_n/\sigma_t$, $\alpha_c$ was decreased to $70 \sim 80\%$ initial $\alpha$ at $\sigma_n/\sigma_t = 0.5$. Though $\alpha_c/\alpha$ depended on $\alpha$, $\sigma_n/\sigma_t$ and the grade of cast iron, $(\alpha_c - 1)/(\alpha - 1) \approx 0.5$ was almost valid at $\sigma_n/\sigma_t = 0.5$.

According to the experiment on FC 25 plates (60 mm × 6 mm section) with a circular hole of 30 mm diameter, the decreasing of $\alpha_c$ almost agreed with the calculated value. The measured $(\alpha_c - 1)/(\alpha - 1)$ was $0.55 \sim 0.6$ at $\sigma_n/\sigma_t = 0.5$. Analysis of the notch sensitivity factor $\eta = (\beta - 1)/(\alpha - 1)$ revealed that the value of $\eta$ larger than 0.5 is due to the non-elastic behavior of cast iron. The additional effect of micro-notches of graphite flake must be considered when $\eta$ is smaller than 0.5. (Japanese)

# Cation Distributions in the Ferrous Sulfide Scales Formed on Binary Iron Alloys

T. Narita and K. Nishida

Denki-Kagaku. **44,** 159 (1976)

Concentration profiles of Cr, Mn, Co, Ni, and Cu in the ferrous sulfide scale on iron based alloys were determined by using EPMA and then analyzed according to the Wagner theory.

In every iron binary alloy used, good agreements were observed between the measured and calculated concentration profiles when the particular values of $P$ $(=D^*_{\mathrm{Fe}}/D^*_{\mathrm{M}})$ were used depending on alloy elements. From these analytical results, it was found that self-diffusivities of each element in the ferrous sulfide scales have the following series in the temperature range from 700 to 900°C:

$$D^*_{\mathrm{Mn}} > D^*_{\mathrm{Cu}} > D^*_{\mathrm{Ni}} > D^*_{\mathrm{Co}} \leqq D^*_{\mathrm{Fe}} \gg D^*_{\mathrm{Cr}}$$

The differences between each pair of these self-diffusivities are considered to be not ascribed to the activation energy of diffusion, but to the pre-exponential term $(D^{*\circ}_{\mathrm{M}})$ in the relation: $D^*_{\mathrm{M}} = D^{*\circ}_{\mathrm{M}} \exp\left(\frac{-Q}{RT}\right)$. These results were discussed on the basis of the Zener theory for self-diffusion. From the present results, it was shown that Wagner's theory was useful in considering the distribution of cations in the sulfide scales. (English)

# On the Atmospheric Oxidation of Pure and Siliconized Ta Metal Sheets at 1000°C

K. Nishida and M. Hachinohe

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 79,** 139 (1976)

With a pure silicon vapor technique Ta sheets were siliconized in an evacuated quartz ampoule up to 49 hr at 1000°C, and then these siliconized sheets as well as untreated ones were oxidized at 1000°C for 15 min in an atmospheric air in order to determine the resistance of siliconized Ta metal against oxidation. Severe oxidation of pure Ta sheets almost prevented by using this method under the above-metioned conditions. Next, the mechanism of this protection process of siliconizing was discussed. (English)

## High Temperature Oxidation of Chromized Ta Sheets

K. Nishida and M. Hachinohe

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 79,** 149 (1976)

In order to improve the anti-oxidation property of Ta metal, metal sheets were chromized at 1000°C up to 144 hr with a pure chromium vapor technique and then the treated metal sheets were examined by oxidizing in air at 1000°C for 15 min. By a comparison between the results of chromizing and siliconizing it was clarified that chromizing of Ta sheets was slower than the latter but even the thin chromized layer improved its oxidation resistance to a greater extent than the thick siliconized layer. (Japanese)

# Some Experiments on the Formation of an Fe-Al Double Sulfide Compound

K. Nishida and T. Narita

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 81,** 99 (1976)

In order to confirm the existence of a special sulfide invariably observed in the scale formed on high Al-ferrous alloys having a good resistance against sulfurization, a double sulfide compound was synthesized with mixed powdered metals of Fe and Al with various ratios in an environment of 1 atm sulfur vapor and under a pure $H_2S$ gas flow. Then the products were examined by X-ray diffraction and chemical analysis.

The constituents of the products were estimated as $FeAl_2S_4$ in mole by numerous experiments although they were different from each other owing to the lack of a good quality of vessels for preparations.

The crystalline structure of the sulfide was determined to be a hexagonal type by many analytical calculations and its lattice parameters were estimated, but from the recent data of Flahaut the recalculated results were $a_0=3.659\pm0.004$ Å; $c_0=36.16\pm0.03$ Å which were very similar to his calculations.

Accordingly, the above stated sulfide was confirmed to be the same as the present compound and was invariably constant even when the original alloys consisted of various constituents. (English)

## Calorizing of Ta Sheets at 1000°C in Al Vapor

K. Nishida and M. Hachinohe

The Journal of the Metal Finishing Society
of Japan, **27,** 665 (1976)

Ta sheets were calorized in a quartz ampoule by using Al vapor generated from the powdered $FeAl_2$ alloy at 1000°C for various durations of pretreatment. The Ta–Al alloy layer formed on the surface was examined by microscopy, X-ray diffraction, and electron probe microanalysis. It was found that the calorizing process of Ta sheets obeyed a parabolic rate law and the rate constant was about one third of that for siliconizing (formation of $TaSi_2$ layer) under the same conditions. The alloy layer formed was mainly of $TaAl_3$ compound and the formation of its layer proceeded through only an inward diffusion of Al, but the transient initial process was found to occur relatively rapidly to form a low Al–Ta alloy layer through the mutual diffusion of both Ta and Al atoms, which was recognized by the existence of Ta oxide particles as the markers. After a long duration of calorizing process (25 hr), the surface of the alloy layer was found to be converted gradually into a low Al–Ta alloy owing to the slight decreases of Al vapor from the powdered Al-source, though the overall kinetics of the process showed no alteration. (Japanese)

# Theoretical Analyses of Cation Distributions in the (Co, Ni) O Scale Formed on Co–Low Ni Alloys

T. Narita and K. Nishida

Transactions of JIM, **17**, 849 (1976)

Concentration profiles of nickel in the (Co, Ni) O scales grown on the Co–low Ni alloys (0.45, 2.46, and 7.23 wt % Ni) over the temperature range from 1000 to 1300°C were determined by means of EPMA and then analyzed according to the analytical equation of Wagner and the differential equations of Dalvi et al.

By making use of both computation methods, the concentration profiles similar to the observed ones were obtained, but the agreement between them was found to be insufficient in the inner part of the scale. The values of $P(=D_{Ni}/D_{Co})$ and $n$ in $P_{O_2}^{1/n}$ determined by the present analytical method were within the range of the literature values. These values of $P$ and $n$ depended on all other parameters, in particular, strongly on $\xi'$ (NiO content at the alloy-scale interface) and $k'$ $(=k/D_{Co}^0)$, respectively. In contrast with the presentation by Dalvi et al., both $P$ and $n$ values changed with NiO content in the oxide.

The mass balance equations at both scale interfaces were used to judge the validity of the numerically obtained solutions. The resulting solutions did not satisfy the mass balance equation at the scale-gas interface. Therefore, it was concluded that the perfect solutions could not be obtained by using the equations of Dalvi et al. This result may be ascribed to the change in the $P$ and $n$ values with NiO content in the oxide.

On the other hand, the equation of Wagner is suitable for an approximate estimation of the cation distribution and diffusivities in the oxide scales because of its simplified form. (English)

# On the Interdiffusion in an FeS-$Cr_2S_3$ System

K. Nishida, T. Narita and A. Notoh

Asahi Garasu Kogyo Shoreikai Kenkyu
Hokoku **29,** 123 (1976)

The mutual reaction between iron sulfide (FeS) and chrome sulfide ($Cr_2S_3$) was investigated through the diffusion experiments with a cramp technique over the temperature range from 600 to 800°C.

It was revealed that the diffusivity of iron into chrome sulfide was higher than that of chrome into iron sulfide, and only the latter was found to depend on the composition of sulfides and to increase with sulfur content (vacancy concentration) in each sulfide.

Interdiffusion coefficients ($\tilde{D}$) and activation energies for diffusion ($\tilde{Q}$) in both sulfides were as follows:
$\tilde{D}(Cr_2S_3)=10^{-8}\sim10^{-10}$ cm²/sec and $\tilde{Q}(Cr_2S_3)=40\sim60$ kcal/mol in $Cr_2S_3$ phase, $\tilde{D}(FeS)=10^{-9}\sim10^{-11}$ cm²/sec and $\tilde{Q}(FeS)=40$ kcal/mol in FeS phase.

From above results it was deduced that the diffusions in both sulfides depended on the vacancy concentrations in them and that they were controlled mainly by the mobility of chrome atoms. (Japanese)

# Permeability of Molten Iron with Nitrogen and Determination of Thickness of Diffusion Layer

K. Atarashiya

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 80,** 113 (1976)

The surface of molten iron in an $Al_2O_3$-cruible was divided into two parts by $Al_2O_3$-tube into which nitrogen and argon could not permeate. One part of the surface was kept in argon atmosphere and the other part was kept in nitrogen atmosphere. Nitrogen which permeates the Ar-side throughout the molten iron was measured. Then, diffusion phenomena of nitrogen were discussed and the following conclusions were obtained.

(1) Permeation rate of Nitrogen was unchanged as the flow rate of argon was rapid. And, a nearly constant value of $D_N/\Delta l$ was obtained. Where, $D_N$ is the diffusion coefficient of nitrogen in molten iron and $\Delta l$ is the thickness of diffusion layer in molten iron. Thus, the rate controlling step of permeation of nitrogen in molten iron is the diffusion process of nitrogen in molten iron.

(2) At 1,600°C~1,630°C,

$$D_N/\Delta l = 2.4\times10^{-2} \sim 5.1\times10^{-2}\ \mathrm{cm/sec}$$

was obtained.

(3) Diffusion coefficient of nitrogen in molten iron is $1.3\times10^{-4}$ $\mathrm{cm^2/sec}$ at 1,600°C then the thickness of diffusion layer in molten iron is $2.5\times10^{-3} \sim 5.4\times10^{-3}$ cm when a high frequency electric furnace is used for melting. (Japanese)

# The Effect of Ferric Hydroxide on the Oxygenation of Ferrous Ions in Neutral Solutions

H. Tamura, K. Goto and M. Nagayama

Corrosion Sci., **16,** 197 (1976)

The oxygenation of $Fe^{2+}$ ions in neutral solutions is accelerated by the reaction product, Fe(III) hydroxide, or by the addition of Fe(III) hydroxide. The reaction proceeds along two paths; one is the homogeneous reaction occurring in the solution and the other is the heterogeneous one taking place on the Fe(III) hydroxide. At constant pH and $O_2$ concentration, the rate is expressed by

$$-d[\mathrm{Fe}^{2+}]/dt = \left(k + k' [\mathrm{Fe(III)}]\right) [\mathrm{Fe}^{2+}].$$

The rate constant $k$ for the homogeneous reaction is equal to $k_0 [O_2] [OH^-]^2$ and $k'$ for the heterogeneous reaction is determined by $k_{s,o} [O_2] K/[H^+]$; $k_o$ and $k_{s,o}$ are the specific rate constants for the two reactions and $K$ is the equilibrium constant for the adsorption of $Fe^{2+}$ on Fe(III) hydroxide. The catalytic effect of Fe(III) hydroxide for the oxygenation is discussed in detail. (English)

# Effect of Anions on the Oxygenation of Ferrous Ion in Neutral Solutions

H. Tamura, K. Goto and M. Nagayama

J. Inorg. Nucl. Chem., **38,** 113 (1976)

The rate of oxygenation of ferrous ions was measured in neutral and slightly acidic solutions containing various anions. The reaction proceeded according to $-d(\mathrm{Fe^{II}})/dt=k(\mathrm{Fe^{II}})(\mathrm{O_2})(\mathrm{OH})^2$ in solutions of $ClO_4^-$, $NO_3^-$, $Cl^-$, $H_3SiO_4^-$, $Br^-$, $I^-$ and $SO_4^{2-}$, the rate constant, $k$, decreasing in the order of anions as arranged above. Anions such as $F^-$ and $H_2PO_4^-$ were found to accelerate the reaction remarkably. The rate equations obtained were $-d(\mathrm{Fe^{II}})/dt=k_F(\mathrm{Fe^{II}})(\mathrm{O_2})(\mathrm{OH^-})(\mathrm{F^-})^2$ and $-d(\mathrm{Fe^{II}})/dt=k_p(\mathrm{Fe^{II}})(\mathrm{O_2})(\mathrm{OH^-})(\mathrm{H_2PO_4^-})^n$. The value of $n$ was 1 or 2 depending upon the concentration of the anion. The role of the respective anions in the oxygenation was explained by assuming that the complex of the anion with ferrous ion is the reacting species. The type of rate equation was shown to be determined by the competition of the complex with $FeOH^+$ for $O_2OH^-$, the dissociated species of hydrated oxygen. (English)

# Topographies of Thick Cu-Benzotriazolate Films on Copper

T. Notoya and G. W. Poling

Corrosion, **32,** (No. 6) 216 (1976)

Topographies of thick copper benzotriazolate (CuBTA) films were examined using scanning electron microscopy. CuBTA films were formed on coarse grained polycrystalline copper in slightly acidic solution containing benzotriazole. The thickness of the underlying $Cu_2O$ and the CuBTA films were estimated from infrared multiple reflection-absorption spectra. Relationships among the structures of the CuBTA films, the $Cu_2O$ interlayers, and the crystallographic orientations of substrate copper crystal faces are described. (English)

# Dissolution of Metal Oxide

M. Seo and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
**25**, 161 (1976) No. 3

The dissolution reaction of metal oxide is directly related to the corrosion of metals, the hydrometallurgy and the acid-pickling of metallic materials. There has been a number of the studies on the dissolution reaction of metal oxide under a variety of environment. This article reviews the dissolution theories of ionic crystals proposed independently by Engell and Vermilyea and their application and limitation to the dissolution of metal oxide. Furthermore, discussion is given to the factors which control the dissolution rate such as the potential distribution at the oxide-solution interface, the semiconducting properties of oxide and the redox and the redox system in the solution. (Japanese)

# Distribution of Anion and Proton across the Barrier Layer of Porous Anodic Oxide Films on Aluminium

M. Nagayama and H. Takahashi

Proc. U.S.–Japan Seminar for Passivity and
Its Breakdown on Iron and Iron Base
Alloys, pp. 56 (Copyright 1975)

It is known that oxide films anodically formed on Al in acid solution contain many parallel pores extending from the outer surface to·the top of a thin "barrier layer". The concentration profiles of phosphate ions and protons across the pore-wall were determined for films formed in a $H_3PO_4$ solution with or without addition of tritium. A technique of dissolving the film in a $H_2SO_4$ solution was utilized. Dissolution proceeds to widen the pores so that we could estimated the distributions from the measurements of the dissolved amounts of phosphate and tritium.

It was found that the phosphate concentration increases gradually with the distance inwards from the surface but decreases steeply to zero as the center of the wall is approached. The concentration of proton, on the other hand, decreases steeply with the distance to attain zero. The distributions of phosphate and proton across the barrier layer are similar to those across the pore-wall; this was ascertained by ESCA and electron microscopy. The mechanism of film growth is discussed to explain the distributions of phosphate and proton. (English)

# Pore-Filling of Porous Anodic Oxide Films on Aluminium

H. Takahashi and M. Nagayama

J. Metal Finishing Soc. Japan, **27,** 338 (1976)

Aluminium specimens anodized to form porous oxide films in an oxalic acid solution were reanodized in a neutral boric acid-borate solution (pH=7.4, 20°C) at a constant c. d. of 0.5 mA/cm$^2$ and changes in the anodizing voltage and geometrical structure of the film were examined. An automatic apparatus was used for the current-controlled electrolysis and an ultra-thin sectioning technique was utilized in electron-microscopy. It was found that the oxide formation occurs both at the barrier oxide/solution and oxide/metal interphases. The former which leads to pore-fiilling is due to the transport of $Al^{3+}$ ions through the barrier oxide whereas the latter is caused by the $O^{2-}$ ion transportation. The voltage-time relationship is represented by two successive straight lines of different slopes and the pore-filling was found to be completed at the time when the slope changes. Apparent transport number for $Al^{3+}$ and $O^{2-}$ ions were determined respectively to be 0.40 and 0.60 and they were almost independent of the applied c. d. It is shown that the porosity and thickness of the film could be estimated by an analysis of the voltage-time relationship using the above transport numbers. (Japanese)

# Determination of Porosity of Anodic Oxide Films on Alumininium by the Pore-Filling Method

H. Takahashi and M. Nagayama

J. Kinki Al Anodizing Soc. No. 63 (1976)

The validity of the pore-filling method proposed by Dekker and Middelhoek to measure the porosity of anodic oxide films on aluminium was verified by electron microscopy on sections of films. The method was somewhat revised in that the pore-filling (or forming) was performed in a neutral boric acid-borate solution ($pH = 7.4$, 20°C) by applying a constant anodic c. d. of 0.5 $mA/cm^2$. Under this condition, the apparent transport numbers for $Al^{3+}$ and $O^{2-}$ ions moving across the barrier oxide layers are found to be 0.40 and 0.60. Using these values of transport numbers, the porosity of oxide was determined for specimens which had been anodized in an oxalic acid solution and thereafter chemically etched for certain periods of time in the same solution. The results obtained are in good agreements with those estimated by electron microscopy. It was recognized that the transport numbers are practically independent of the nature of anodizing solution, anodizing c. d. and the forming c. d. to fill the pores. (Japanese)

# General Theory of Metal Passivity

## ——Passivity of Iron, Nickel and Cobalt——

N. Sato

Corrosion Engineering (Boshoku Gijutsu),
**25,** 35 (1976) No. 1

Recent contributions to the passivity of iron and iron-base alloys were reviewed, and the anodic current-potential and film thickness-potential curves of iron, nickel and cobalt were shown along with the discussions of ionic current in and dissolution current of the passive film. There is a barrier oxide layer on the surface of passivated metals. For iron it is an iron-deficient magnetite layer, for nickel a layer of NiO with excess oxygen, and for cobalt a bi-layer of $CoO/Co_3O_4$. The ionic current in the barrier oxide layer on iron and in the outer barrier $Co_3O_4$ layer on cobalt obeys a field-assisted ion migration mechanism. This mechanism, however, does not hold for the barrier NiO layer on nickel and the inner CoO layer on cobalt. The dissolution current of the passive film is controlled by the potential difference across the Helmholtz layer at the film/solution interface, and a Tafel relation is found to hold between the film dissolution current and the overpotential at the Helmholtz layer, leading to the mechanism for iron as $Fe^{3+}$ (oxide)$\rightarrow$$Fe^{3+}$ (solution) and for cobalt as $Co^{2+}$ (oxide)$\rightarrow$$Co^{2+}$ (solution). A generalized theory was presented in which the metal passivity was attributed to the involvement of a thin oxide film into the structure of electrified interface between the metal and the solution. The passive film formed on a metal changes the electrical double layer at the metal/solution interface into a bi-layer structure consisting of a thin oxide layer and the Helmholtz layer at the film/solution interface, and thus the effective overpotential for metal ion transfer scross the Helmholtz layer is reduced resulting in a decrease of metal dissolution rate. (Japanese)

# The Potential Dependence of Composition of Anodic Passive Film on Iron in Neutral Solution

R. Nishimura, K. Kudo and N. Sato

Journal of the Japan Institute of Metals,
**40,** 118 (1976) No. 2

The composition of anodic passive film on iron in a neutral borate-buffer solution at pH 8.42 has been studied as a function of potentials ranging from passivation to transpassivation by using ellipsometric and electrochemical techniques.

Ellipsometric measurements reveal that there are three different potential regions with respect to the $\Delta P - \Delta A$ relationship, i. e. a region more cathodic to +0.245 V (S. H. E.) (region I), a region from +0.245 V (S. H. E.) to the oxygen evolution potential (region II) and a region of transpassivity (region III). It is also found that the anodic passive film consists of a barrier layer and a deposit layer.

The barrier layer thickness increases linearly with the passivating potential in region I and region II, whereas it appears independent of anodic potential in region III. The deposit layer thickness is affected to some extent by the anodic potential.

The film dissolution measurements by means of cathodic reduction in a solution of pH 6.48 at constant current indicate that the film formed in region I includes $Fe^{2+}$ ions in both the barrier layer and the deposit layer, while the film formed in region II includes no $Fe^{2+}$ ions in both layers. The film formed in region III contains no $Fe^{2+}$ ions in the deposit layer but it contains $Fe^{2+}$ ions in the barrier layer. Furthermore, there is a layer of concentrated $Fe^{2+}$ ions at the interface between the barrier layer and the deposit layer in the film formed at potentials more cathodic to +0.8 V (S. H. E.), whereas a depletion layer of iron ions is formed at the barrier/deposit interface at potentials more anodic to +0.8 V (S. H. E.). (Japanese)

# Galvanostatic-cathodic Reduction of the Passive Films on Iron in Neutral Boric-borate Solutions

R. Nishimura, K. Kudo and N. Sato

J. Electrochem. Soc. Japan (Denki Kagaku),
**44,** 198 (1976) No. 3

The passive films formed on iron in a borate-buffer solution at pH 8.42 were electrochemically reduced at a constant cathodic current in borate solutions of pH values ranging from 6.48 to 8.42, and the current efficiency for the cathodic dissolution of the film were measured.

At pH 8.42 the usual method using a continuous cathodic current let to a current efficiency of less than 100%, but the application of a current pulse allowed to be reduced at 100% current efficiency.

Under continuous cathodic current, some of the reduction product $FeOH^+$ in the area where the diffusion layer of the solution was in contact with film surface changed, due to supersaturation with ferrous ions, to a hydrous ferrous oxide deposit which was eventually reduced to metallic iron. The application of cathodic current pulses at a proper interval prevented ferrous ion saturation of the diffusion layer thus leading to the complete dissolution of the passive film without any side reaction during reduction.

At pH 6.48, a current efficiency of 100% was obtained even with a continuous cathodic current, probably because of the extremely large saturation concentration of $[FeOH^+]$ obtained from the solubility product of the reaction $FeOH^+ + OH^- \rightleftharpoons Fe(OH)_2$.

It was found that in cathodic reduction the passive film formed at low potential included ferrous ions, whereas all the iron ions in the film formed at high potential were ferric. (Japanese)

# Cathodic Reduction of Passive Films on Iron

R. Nishimura, K. Kudo and N. Sato

J. Electrochem. Soc. Japan (Denki Kagaku),
**44,** 518 (1976) No. 8

The effects of solution pH and cathodic current density on the cathodic reduction of passive films on iron have been investigated to elucidate the mechanism of the cathodic dissolution of the films.

Cathodic reduction produces ferrous ions ($FeOH^+$) in the solution. Current efficiency $\eta$ for the cathodic dissolution, obtained from $W_{Fe^{2+}}-Q_c$ curves, is shown to decrease linearly with increases of solution pH between 6.35 and 10.05. At constant solution pH, $\eta$ appears to be almost independent of cathodic current density, *i.e.* $\eta \doteqdot 0.8$ at pH 8.42.

These results are interpreted by assuming that the ratio of the number of $FeOH^+$ ions diffusing into the bulk solution to the number precipitating as ferrous hydroxide in a surface solution layer increases as solution pH decreases.

The potential decay during cathodic film dissolution exhibits at least two potential plateaux which depend on solution pH and cathodic current density. The first plateau corresponds to the reduction $Fe(OH)_3+2H^+ + e \rightleftharpoons FeOH^+ + 2H_2O$ or $1/2\gamma\text{-}Fe_2O_3+2H^+ + e \rightleftharpoons Fe\ OH^+ + 1/2\ H_2O$, and the second to the cathodic evolution of hydrogen and the reduction of ferrous hydroxide to metallic iron. (Japanese)

# Intensity-Following Ellipsometry of the Passive Film on Iron

R. Nishimura, K. Kudo and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
**25,** 83 (1976) No. 2

An improved intensity-following method of ellipsometry which allows continuous measurements of ellipsometric parameters to be made of changing surfaces is described and applied to measurements of the passive film on iron. The merits of this method are as follows, (1) it can be used not only for case of small incidence angle but also for the case of large incidence angle in which the change of $P$ and $A$ due to the film formation is usually large, (2) it is not affected by the initial light intensity which often differs with different measurements, and (3) only two successive measurements instead of three runs with conventional method are required to estimate ellipsometric parameters $P$ and $A$. The method was used to measure the passive formed on iron in a sodium borate solution at pH 8.42 and its cathodic reduction at pH 6.48 at which the film can be reduced layer by layer without changing its composition. For the steady state film there are three different potential regions in the $\Delta P-\Delta A$ curve with respect to its slope; the first region corresponds to the films formed in the potential region between $-0.3$ V and $+0.245$ V, the second region to those formed between $+0.245$ V and $+1.54$ V and the third region to those formed above $+1.54$ V. From cathodic reduction measurements, it is found that the passive film consists of two layers, an inner barrier layer and an outer deposit layer. The optical constants of the barrier layer, calculated from the slope of $\Delta P-\Delta A$ curve obtained during cathodic reduction, differ with different film formation potentical regions described above. The optical constants of the deposit layer, however, scarcely change with the film formation potential except for a potential

region below +0.245 V. From comparison of the optical constants of the passive film with those of known iron oxides and hydroxides, the deposit layer is estimated to be an amorphous hydroxide and the barrier layer to be an oxide close to $\gamma$-$Fe_2O_3$. (Japanese)

# Depth Analysis of Passive Films on Iron in Neutral Borate Solution

N. Sato, K. Kudo and R. Nishimura

J. Electrochem. Soc., **123,** 1419 (1976), No. 10

Composition depth profiles of passive films on iron in a borate solution at pH 8.42 have been obtained by means of cathodic reduction combined with ellipsometry and chemical analysis. Results revealed that the compositional profile varied depending primarily on the potential and to some degree on the time of film growth. The barrier layer in contact with the metal changed in composition from an iron (II–III) mixed oxide at potentials below the Flade potential to an iron (III) oxide at more noble potentials. The deposit layer next to the solution was a hydrated iron (III) oxide and absorbed iron (II) ions at less noble potentials. There was found a perk or a decrease in iron concentration at the barrier/deposit boundary. The iron-rich boundary was gradually replaced by the iron-depleted as the potential was shifted to more noble direction. It was the barrier layer alone that increased in thickness during the film growth at potentials above the Flade potential. In the transpassive potential region the barrier layer ceased growing with potential and tended to contain a small concentration of iron (II) ions. It is suggested that the ion transport in the layers plays a role in determining the passive film composition. (English)

# Thickness and Layer Structure of Anodic Passivating Films on Cobalt in Neutral Solution

T. Ohtsuka, K. Kudo and N. Sato

Journal of the Japan Institute of Metals
**40,** 124 (1976), No. 2

The thickness and layer structure of the passive film formed on cobalt by potentiostatic oxidation in a borate-buffer solution of pH 8.42 have been studied by ellipsometry, electrochemical techniques and chemical analysis. The primary passive film is formed in a potential region from $-0.05$ to $+0.37$ V (vs SHE) where the steady dissolution current of cobalt is about 2 $\mu$A/cm$^2$ almost independent of the potential. This film is composed of CoO with the complex refractive index $N=2.3-0.1\ i$ and the thickness which increases from 20 to 25 Å with rising potential. The secondary passive film is formed at potentials more positive than 0.4 V, where the steady dissolution current is less than 0.1 $\mu$A/cm$^2$. It consists of an inner layer of CoO with the refractive index $N=2.3-(0.1\sim0.3)\ i$ and an outer layer of oxide of either $Co_3O_4$ or $Co_2O_3$. Transition from $Co_3O_4$ to $Co_2O_3$ occurs in a potential region from 0.72 V to 0.95 V. The refractive index of the outer layer was estimated as $N=3.2-0.5\ i$ for $Co_3O_4$ and $N=3.2-0.95\ i$ for $Co_2O_3$. The thickness of the outer layer increases almost linearly with the potential up to 37 Å at $+1.15$ V and remains constant in a potential region more positive than $+1.15$ V, where the transpassive dissolution occurs. The inner layer layer of CoO also increases with potential but has a maximum thickness of about 40 Å at $+0.8$ V around which the transition from $Co_3O_4$ to $Co_2O_3$ occurs. (Japanese)

# Stochastic Process of Chloride Pit Generation in Passive Stainless Steel

N. Sato

J. Electrochem. Soc., **123,** 1197 (1976), No. 8

The present paper describes an application of the theory of the Markov process to potentiostatic pit generation in a rotating stainless steel electrode in an acid solution containing sulfate and chloride ions. The pit generation probability increases and appears to approach a ceilling asymptotically as the potential becomes more noble. In view of stochastic process, the critical potential for pit generation may be defined as the least noble potential at which the pit generation probability is practically recognizable. (English)

# Pitting Corrosion as a Stochastic Process

T. Shibata and T. Takeyama

Nature, **260,** 315 (1976)

A stochastic theory originally developed to explain the fructure of solid materials under stress was proved to be useful in understanding the initiation of pitting corrosion. Since the stochastic approach requires the measurement of several series of data taken in the same controlled conditions, a multichannel pitting corrosion tester has been developed. As predicted by the stochastic theory, the survival probability, $P(t)$, which is defined as the number of non-pitted specimen at time $t$, is described by

$$P(t)=\exp\left(-\int_o^t \lambda(t)\,dt\right)$$

where $\lambda(t)$ is the transition probability depending on the potential and time. The analysis of data based on the above equation suggests that three successive processes are included in pit initiation at a constant potential, and only the first process could be detected by the potential sweep method. The theory also could explain the dependence of the pitting potential against the square root of potential sweep velocity. Furthermore it is pointed out that the lowest pitting potential can be expected on the largest area of specimen. This could explain the unexpected failures which often occur in practical large scale apparatus in spite of proved resistance in laboratory tests using small area specimens. (English).

# Stress Corrosion Cracking of Titanium in Methanol-Iodine Solutions

T. Shibata, T. Takeyama and M. Kurita

Bulletin of the Faculty of Engineering,
Hokkaido University **80,** 93 (1976)

Stress corrosion carcking of titanium was studied in 0.5 wt % iodine in methanol solution by measuring the time to fracture and fractgraphy by scanning electron microscope. Increase of tensile stress applied to the surface specimens by bending is found to decrease the time to fracture, and also alter mode of fracture from an intergranular cracking to a transgranular carking. The transgranular cracking surface shows a very characteristic feature consisting of fluted striations parallel to the direction of crack propagation. A small portion of the transgranular carcking surface contains a pseudocleavage surface. Intergranular cracking may be a kind of stress-assisted corrosion cracking. The velocity of transgranular cracking ($=3.33\times10^{-4}\,\mathrm{cm\cdot sec^{-1}}$, or equivalent dissolution current of $9.07\,\mathrm{A\cdot cm^{-2}}$) is two orders of magnitude higher than the intergranular carcking velocity ($=1.85\times10^{-6}\,\mathrm{cm\cdot sec^{-1}}$, or equivalent dissolution current of $50.4\,\mathrm{mA\cdot cm^{-2}}$). Anodic dissolution model according to the tunnel formation mechanism is suggested to account for the transgranular cracking. (Japanese)

# Plastic Deformation and Reactivity of Passive Metals

T. Shibata and T. Takeyama

"Passivity and its Breakdown on Iron and Iron
Base Alloys" pp. 165, NACE (1976)

An analytical expression was proposed to analyze an intrinsic anodic activity and repassivation process on a freshly generated surface at a passive state because of their inportant role in the stress corrosion cracking phenomena. The equation formulated by considering the generation of fresh surface and also the repassivation is simply reduced to

$$i = d\Delta I/d\Delta S = i^* g/(1+n)$$

when an approximation of $d\Delta I/d\Delta S \simeq \Delta I/\Delta S$ is satisfied experimentally. Where $\Delta I$ is the total current increase when the surface area increment, $\Delta S$, is applied. Thus, the apparent anodic activity, $i$, includes the intrinsic activity, $i^*$, a repassivation prameter, $n$, and a geometric parameter, $g$, which depends on the amount of strain and straining rate. Based on the equation proposed anodic activity and repassivation parameter were determined in 1 N $H_2SO_4$ at 25°C for various iron-chromium- nickel alloys with changing nickel contents. Specific activity which does not include the repassivation prameter was found to increase with increase in iron content in the alloy. Short discussion on the mechanism of SCC is given by considering the parrameters thus determined. (English)

# The Mechanism of Electrodeposition of Copper from Copper Pyrophosphate Solutions Containing Ammonia

H. Konno and M. Nagayama

J. Metal Finishing Soc. Japan, **27,** 135 (1976)

An investigation has been made of the electrodeposition of copper from solution of $Cu(P_2O_7)_2^{6-}$ containing small amounts of ammonia. It is found that mixed complex ions, $Cu(P_2O_7)(NH_3)^{2-}$ and $Cu(P_2O_7)(NH_3)_2^{2-}$, are formed at small concentrations in the solution, and hence the possible deposition reactions are:

$$\left.\begin{array}{l} Cu(P_2O_7)_2^{6-} \rightleftarrows Cu(P_2O_7)^{2-} + P_2O_7^{4-} \\ Cu(P_2O_7)^{2-} + 2e \rightarrow Cu + P_2O_7^{4-} \end{array}\right\} \text{(Main)} \qquad (1)$$

$$\left.\begin{array}{l} Cu(P_2O_7)(NH_3)^{2-} + 2e \rightarrow Cu + P_2O_7^{4-} + NH_3 \\ Cu(P_2O_7)(NH_3)_2^{2-} + 2e \rightarrow Cu + P_2O_7^{4-} + 2NH_3 \end{array}\right\} \text{(Secondary)} \qquad \begin{array}{c}(2)\\(2')\end{array}$$

The increase in cathodic current caused by addition of ammonia is attributed to the secondary reactions occuring parallel with the main reaction (1). The partial current of the secondary reactions was measured by using a rotating copper disc electrode and it was found that the current is proportional to the $Cu(P_2O_7)(NH_3)^{2-}$ ion concentration. This indicates that, of the two secondary reactions, (2) is much more importance. The mechanism of the reaction (2) is discussed in detail and also compared with the one reported previously for the solutions free from ammonia. (Japanese)

# Structure and Composition of Electrodeposited Copper from Copper Pyrophosphate Solutions

H. Konno and M. Nagayama

J. Metal Finishing Soc. Japan, **26,** 582 (1975)

Cathodic current-potential curves were measured for copper electrode in copper pyrophosphate solutions at a pH of 8.5. The deposited copper was examined by means of electron probe micro-analysis, scanning electron microscopy and X-ray diffraction techniques. The cathodic polarization characteristics revealed that the amount of pyrophosphate ion adsorption decreases with increasing cathodic polarization and it becomes almost zero beyond the critical potential of $E_b$ (ca. $-0.7$ V vs. SCE). As could be expected, the phosphorus content in the deposit was relatively high (0.07∼0.05%) in the potential region I which is less negative than $E_b$, and it was low (∼0.02%) in the region II which is more negative than $E_b$. Smooth, semibright deposits were always obtained when the potential was in the region I and current was larger than about 5 mA/cm$^2$. The smooth deposit exhibited random orientation and main peaks were of (111), (200), (220) and (311). On the contrary, rough deposits obtained in the region II showed strong preferred (220) orientation and it is consistent with the preferred orientaion theory. The deposition of a semibright layer in the region I is explained as being due to the pyrophosphate adsorption which prevents surface migration of ad-atoms (or ad-ions) and hence the preferred orientation of crystals. (Japanese)

# Ion-Selectivity of Nickel Chromate, Melybdate, and Tungstate Precipitate Membranes

M. Sakashita and N. Sato

J. Electrochem. Soc. Japan (Denki Kagaku),
**44,** 395 (1976) No. 6

The ion-selectivity of chromate, molybdate, and tungstate precipitate membranes of nickel has been examined by measurements of the membrane potential and polarization behavior. The membranes have been estimated to be cation-exchangers of low fixed charge densities from a comparison between experimental and theoretical membrane potentials according to the fixed charge theory in mono-monovalent electrolyte solutions. In electrolyte solutions of di- and tri-valent cations, the membranes became anion-selective. The order of cation selectivity of the membranes in chloride solutions incerased as $Al^{3+} < Ba^{2+} < Ca^{2+} \leq Mg^{2+} < Li^{+} < Na^{+} < K^{+}$. The increas-ing order of co-ion transport through the membranes was $SO_4^{2-} < ClO_4^{-} < NO_3^{-} < Cl^{-}$. From the polarization behavior, it was estimated that $Ni^{2+}$, $CrO_4^{2-}$, $MoO_4^{2-}$, and $WO_4^{2-}$ ions which constituted the membranes were much less permeable than $Na^{+}$ and $Cl^{-}$ ions. Furthermore, it has been discussed that the surface precipitate film containing $CrO_4^{2-}$, $MoO_4^{2-}$, or $WO_4^{2-}$ acts as a protective film against corrosion of underlying metals because of its ion-selective property. (English)

# Ion Selectivity of Chromium Hydroxide and Chromium-Nickel Mixed Hydroxide Precipitate Membranes

M. Sakashita and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
**25,** 3 (1976) No. 1

Measurements of membrane potentials arising across chromium hydroxide and chromium-nickel mixed hydroxide precipitate membranes have been carried out to estimate the ion selectivity. The chromium hydroxide precipitate membrane showed a high selectivity for anions in electrolyte solutions of neutral pH. The transport number of anions was evaluated to be 0.96–0.95 in sodium chloride, nitrate, and perchlorate solutions. The fixed ion concentration on the membrane characterizing anion exchanger was determined to be about 0.1 g-equiv./*l* by comparing the experimental membrane potentials with the theoretical values derived from the fixed charge theory of membranes. In sodium hydroxide solution, the transport number of $OH^-$ ions through the membrane was not constant but increased with decreasing solution pH. The order of the selectivity for anions determined with the biionic potentials across the chromium hydroxide precipitate membrane was $Cl^- > Br^- > NO^-_3 > I^- > ClO_4^-$. This order of the selectivity significantly from the selectivity for the nickel hydroxide precipitate membrane. The biionic potential across the mixed hydroxide precipitate membranes of chromium and nickel shifted from that of nickel hydroxide to that of chromium hydroxide as the chromium concentration increased. The anion permeability estimated from the membrane potential arising across the biphase hydroxide membrane was very much smaller for the chromium hydroxide than for the nickel hydroxide precipitate membrane. This suggests that chromium is enriched on the surface of hydroxide particles constructing the mixed membranes. (English)

# The Disposal of Waste Water from Laboratory

N. Nagayama, H. Tamura and H. Konno

Bulletin of Japan Institute of Metals,
**15,** 697 (1976)

Waste water from laboratories contains various harmful substances, for example, heavy metal ions, toxic anions, organic compounds, and waste solvents and oils. These substances must be removed or decomposed before discharge into a river or a sewer; the permitted concentrations are established by law. Most heavy metal ions (Cd, Pb, Cu, Zn, Mn, Fe) are removed as hydroxides, by neutralyzing with alkali after decomposing, or oxidizing the coexisting complexing agents; CN is decomposed with $Cl_2$, and organic ligands with $Cr_2O_7^{2-}$. The excess $Cr_2O_7^{2-}$ is reduced to $Cr^{3+}$ with $Fe^{2+}$ and is precipitated as Cr(III) hydroxide. Hg and Ag are removed as sulfide; due to coprecipitation the removal is assisted by the addition of Fe(III) hydroxide. As and F (removed as $CaF_2$) also coprecipitate with Fe(III) hydroxide. The separation of these precipitates from water is facilitated by letting the precipitates grow large. This is effective to speed up sedimentation, make filtration easier and keep the precipitated volume small. To obtain a precipitate of large particles, it is recommended to work with reasonably dilute waste water adding alkali slowly at above room temperatures and let the precipitate thus formed stand for aging. Further, it is shown that if different kinds of waste water is mixed, good results are obtained due to interactions between the waste materials (acid-base and redox reactions and coprecipitation). Waste solvents and oils are burnt or decomposed in a special furnace equipped with an exhaust gas scrubber. As an example, the system and the methods at Hokkaido University for the disposal of waste water are described in detail. (Japanese)

# Determination of Cyanide by Silver Titration Method

H. Konno, N. Nishitani and M. Nagayama

J. Metal Finishing Soc. Japan, **27,** 414 (1976)

A silver titration method for free cyanide in aqueous solutions was developed by using a mixed indicator of p-dimethyl-amino-benzylidene-rhodamine (DABR) and thymol phthalein complexon (TPC). 0.2 ppm $CN^-$ was determined with an error of about 2% by 0.001 M $AgNO_3$ titration in the presence of 0.1 mM DABR+0.3 mM TPC. The presence of 10 ppm $Cr^{3+}$, $Fe^{3+}$, $Zn^{2+}$, $Pb^{2+}$ or $Cd^{2+}$ does not interfere with this method. Interference from $Cu^{2+}$, $Ni^{2+}$ and $Hg^{2+}$ can be avoided by preliminary distillation in the usual way. (Japanese)

# A Study for Effective Utilization of Hydrogen Sulfide (2nd Report)

H. Kiuchi, T. Iwasaki, and T. Tanaka

Joural of the Mining and Metallurgical Institute
of Japan, **92,** 212 (1976) No. 1057

The object of this study is to recover $H_2$ from $H_2S$ with molten metal.

The reaction was investigated by two methods of circulation and single-stage blowing of $H_2S$ through molten metal over the temperature range of 380～790°C.

As molten metal, Pb, Sn, and Bi were used owing to other low melting points.

It was found that the conversion of $H_2S$ to $H_2$ by molten Sn, Pb, or Bi decreases in that order.

Hydrogen generation was accelerated by the addition of Ni to molten metal. This acceleration may be due to catalytic action of Ni dissolved in molten Pb. In addition, for molten Bi, it may be responsible for preferential sulfurization of dissolved Ni. (Japanese)

# Treatments of Sulfide Ores Through Hydrogen

T. Tanaka, H. Kiuchi and R. Shibayama

The 24th Non-Ferrous Extractiv Metallugy
Research Meeting Data, **1,** 24, (1976)

A few opinions on the treatment of sulfide ores mainly through hydrogen were stated. Development of hydrogen problem in energy field fully contains and a possibility of an important problem affecting the basis of present extractive metallurgy. As a future direction, a way reconsidering the treatment of sulfide Ores, not only from the side of metallurgy, but also from the based on chemical characteristics and physical properties of sulfur will be required. When we look at the recent research examples on the utilization of sulfur, they are broadly related to the whole engineering, and "Sulfur Chemistry" furthermore "Sulfur Engineering" trend is increasing. Accordingly, treatment of sulfide one should be collectively grasped including the utilization of hydrogen and sulphur as a part of "Sulfur Engineering", and not from the viewpoint of extractive metallurgy only. Further, as one of directions for the solution of important themes such as translation toward the low quality energy type metallurgy in the future energy conservation society, or exploitation of unused low quality ore to correspond with the exhaustion of metal resources, application of hydrogen should be considered positively in the future. Also, such a course may lead to the development of new metallurgical process in the future. (Japanese)

# Preparation of Aluminum Nitride Films by Reactive Sputtering

Y. Hirohata, T. Abe and T. Yamashina

J. Appl. Phys. of Japan **45,** 402 (1976)

Aluminum nitride films ($AlN_x$) containing various amount of nitrogen were prepared by an R. F. reactive sputtering. The deposition rate, electrical resistivity, crystal structure and chemical composition were observed systematically on the sputtered film prepared under the nitrogen partial pressures ranging from $1\times10^{-4}$ to $2.5\times10^{-2}$ Torr in argon-nitrogen mixed gas (total pressure was $2.5\times10^{-2}$ Torr).

The deposition rate of the films was found to decrease drasstically at a critical partial pressure of nitrogen, $4\times10^{-3}$ Torr, while the resistivity of films began to increase gradually over the same critical pressure. X-ray diffraction measurement of the films prepared under various pressures of nitrogen was carried out. It was found that the structure of the films also began to change in the region of the critical pressure, namely, only the diffraction pattern from metallic Al was observed for the nitrogen partial pressures below $6\times10^{-3}$ Torr, then the diffraction pattern from AlN began to appear over $6\times10^{-3}$ Torr. Chemical composition of the film determined by X-ray microanalysis shpwed the change corresponding to that of the crystal structure with the nitrogen pressure.

On the basis of the experimental data, discussion was made on the change of deposition rate of the films with nitrogen pressure by a theoretical model for the sputtering process of targest surface, and on correlation between the electrical resistivity and the crystal structure of the sputtered films. (Japanese)

# AES-FDS Simultaneous Measurement for Decomposition of Formic Acid over Clean Surface of Copper-Nickel Alloy

K. Watanabe, M. Mohri, M. Hashiba
and T. Yamashina

Chem. Lett., 1343 (1976)

A combined system of Auger spectroscopy (AES) and fiash desorption spectroscopy (FDS) was utilized to reveal adsorption and decomposition processes of formic acid over clean surface of Cu-Ni alloy. It was found that the surface treatments of ion-bombardment and annealing brought about a great difference in decoposition process which could be attributed to change of the surface composition. (English)

# Measurement of Sorption Rate for Nitrogen by Zirconium at Elevated Temperature

M. Nagasaka

J. Vac. Sci. Technsl., **13,** 676 (1976)

A study has been made of sorption rate for nitrogen by zirconium in the range of $10^{-2}$ $-10$ Pa and 600°～850°C by means of the constant-volume method. Depending on nitrogen pressure, two types of rate law were observed; i.e., the linear and parabolic rate laws in the range of lower and higher pressure, respectively. The properties of nitrogen sorption under the constant-volume condition are discussed by use of Wagner's model involving simultaneous formation of compact scale and the dissolution of nitrogen atoms into the metal bulk. (English)

# A Quantitative Analysis of Surface Segregation and In-depth Profile of Copper-Nickel Alloys

K. Watanabe, M. Hashiba and T. Yamashina

Surface Science **61,** 483 (1976)

By utilizing the difference in escape length of the Auger electrons with different energies, a calculation of the in-depth distribution of atomic concentration at the surface is presented on the basis of Palmberg's physical mechanism. Experimental results on clean surfaces of Cu–Ni alloys over the entire composition region with Auger spectroscopy were performed to make the in-depth profile of surface composition casused by annealing. The alloy composition of the first atomic layer at the surface was plotted against the bulk composition, showing significant enrichment of Cu atoms in the layer. The results indicated that the segregation takes place in about four atomic layers at the surface. (English)

# Solubility of Hydrogen and Deuterium in Titamium and Zirconium under Very Low Pressure

M. Nagasaka and T. Yamashina

Journal of the Less-Common Metals
**45,** 53 (1976)

The solubilities of hydrogen and deuterium in $\alpha$-titanium (500～800°C), $\beta$-titanium (900～1150°C) and $\alpha$-zirconium (500～800°C) were determined in the pressure range $10^{-4}$～$10^{-2}$ Torr, using an UHV apparatus. The solubility data were observed to obey Sieverts' law exactly. The isotop effect of hydrogen and deuterium on the solubility in the $\alpha$-phase of titanium and zirconium could be explained by applying McLellan's model. The previous data on the solubility of hydrogen and deuterium in these metals under low pressure were comprehensively compared. (English)